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THE KINETICS OF THE GAS PHASE REACTION OF NITROUS ACID WITH OZO--ETC(U)

JUL 77 E W KAISER, S M JAPAR

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10 E. W. Kaiser S. M. Japar



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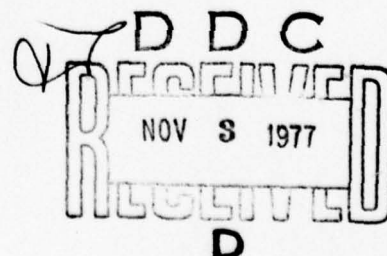
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16. Abstract <p>The kinetics of the gas phase reaction between ozone and nitrous acid have been investigated under conditions applicable to the middle stratosphere. The decay of nitrous acid (<0.005 Torr) in the presence of excess ozone (0.4-14 Torr) has been measured at 226° and 300° K using a mass spectrometer detector. At both temperatures, the observed decay rate is independent of ozone concentration and apparently arises from heterogeneous reactions, rather than from the homogeneous bimolecular reaction (1),</p> <p><i>Reaction coefficient</i> $\text{HNO}_2^M + \text{O}_3^M \xrightleftharpoons{K} \text{HNO}_3^M + \text{O}_2^M \quad (1)^* \quad \text{yields}$</p> <p>Conservative upper limits to the value of K, calculated by assuming that the entire HNO_2 decay results from reaction (1), are 1×10^{-19} and 5×10^{-19} $\text{cm}^3/\text{molecule-sec}$ at 300° and 226° K respectively. Calculations based on a simplified mechanism for stratospheric NO_x chemistry indicate that reaction (1), with a rate constant of the magnitude reported above, is unlikely to be important in the chemistry of the stratosphere.</p> <p><i>Chcm</i> <i>from 1 to 5 times 10 to the -19 power</i></p>			
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PREFACE

We wish to express our appreciation to H. Niki for his sound advice during these experiments.

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I. Introduction

In recent years the chemistry of the stratosphere has been studied in detail⁽¹⁾ because of possible perturbations on that chemistry by anthropogenic pollution sources such as the SST,⁽²⁾ nuclear weapons testing in the atmosphere,⁽³⁾ and the use of chlorofluorocarbons.⁽⁴⁾ The main stratospheric constituent, in terms of environmental impact on Earth, is ozone, and below about 45 km the concentration of stratospheric ozone is coupled very strongly to the NO_x chemistry cycle.⁽⁵⁾ The basic reactions in the postulated NO_x cycle^(1,2) are summarized in Table 1. Schiff⁽⁵⁾ has recently assessed the importance of reactions (1) and (2) in the overall cycle. These reactions involve the formation of nitric acid and nitrous acid by paths previously considered unimportant. If the rates of these reactions are large, Schiff has demonstrated that they can markedly reduce the stratospheric concentrations of NO, NO₂ and HNO₂ by converting them to HNO₃, which is much less reactive in the atmosphere. This, in turn, could affect the stratospheric ozone balance to a degree dependent on the magnitude of the rate constants for reactions (1) and (2). An estimate of the rate constant for reaction (2), which is an order of magnitude below the upper limit employed by Schiff,⁽⁵⁾ has recently been published.⁽⁶⁾ The only discussion of reaction (1) in the literature is a statement by Cox⁽⁷⁾ that "... (parts per million) levels of O₃ and HNO₂ do not react at a measurable rate over a period of hours." We have carried out experiments to determine the rate of this latter reaction under conditions applicable to the stratosphere. The results of these measurements will allow a better assessment of the importance of reactions (1) and (2) in stratospheric chemistry.

II. Experimental

The experimental apparatus is presented schematically in Fig. 1. The reactions were carried out in a 1-liter Pyrex reactor located inside an evacuated chamber. The reactor was equipped with a multi-holed glass inlet tube and a thermocouple well. The contents of the reactor were sampled through a 0.05 mm diameter nozzle orifice located at the apex of a cone. The resultant molecular beam first passed into the reactor chamber (pressure $\sim 5 \times 10^{-5}$ Torr) where it was modulated by a tuning fork chopper operated at 400 Hz. It then entered the detector chamber (pressure $\sim 2 \times 10^{-8}$ Torr) which contained an electron impact ionizer coupled to the quadrupole mass analyzer. The ionizer was operated at an electron bombardment energy of 50eV during the experiments.

Table 1 - Rate Constants and Concentrations for Reactions Involved in Stratospheric NO_x Chemistry

Reaction	Rate Constant (cm ³ molecule ⁻¹ sec ⁻¹)		Reference
	22 km*	30 km**	
(1) HNO ₂ + O ₃ = HNO ₃ + O ₂			
(2) HO ₂ + NO ₂ = HNO ₂ + O ₂	2.0 x 10 ⁻¹²	2.0 x 10 ⁻¹²	(a)
(3) NO + O ₃ = NO ₂ + O ₂	3.7 x 10 ⁻¹⁵	4.4 x 10 ⁻¹⁵	(c)
(4) NO ₂ + O = NO + O ₂	9.1 x 10 ⁻¹²	9.1 x 10 ⁻¹²	(c)
(5) NO ₂ + hν = NO + O	7.0 x 10 ⁻³ sec ⁻¹	7.0 x 10 ⁻³ sec ⁻¹	(d)
(6) NO + OH \xrightarrow{M} HONO	1.3 x 10 ⁻¹²	4.8 x 10 ⁻¹³	(c)
(7) NO ₂ + OH \xrightarrow{M} HNO ₃	1.5 x 10 ⁻¹²	7.8 x 10 ⁻¹³	(b) page 5-114
(8) HNO ₂ + hν = NO + OH	6.5 x 10 ⁻⁴ sec ⁻¹	6.5 x 10 ⁻⁴ sec ⁻¹	(f)
(9) HNO ₃ + hν = NO ₂ + OH	4.1 x 10 ⁻⁷ sec ⁻¹	3.5 x 10 ⁻⁶ sec ⁻¹	(b) page 5-117
(10) HNO ₃ + OH = H ₂ O + NO ₃	1.3 x 10 ⁻¹³	1.3 x 10 ⁻¹³	(c)
(11) HO ₂ + NO = NO ₂ + OH	2.0 x 10 ⁻¹³	2.0 x 10 ⁻¹³	(c)

* T = 218°K; M = 1.3 x 10¹⁸ molecules cm⁻³

** T = 226°K; M = 3.8 x 10¹⁷ molecules cm⁻³

Species

	Density (cm ⁻³)		
O ₃	8 x 10 ¹²	3 x 10 ¹²	(e)
O	4 x 10 ⁶	6 x 10 ⁷	(b) page 3-91
OH	8 x 10 ⁵	2 x 10 ⁶	(b) page 3-95
O ₂ H	1 x 10 ⁷	1 x 10 ⁷	(b) page 3-96

Table 1 - (continued)

References

- (a) Reference 5
- (b) Reference 1b
- (c) "Chemical Kinetic and Photochemical Data for Modelling Atmospheric Chemistry," NBS Technical Note 866, R. F. Hampson, Jr. and D. Garvin, Eds., U. S. Department of Commerce (June, 1975).
- (d) Reference 2
- (e) "A proposed midlatitude ozone model for the U.S. Standard Atmosphere 1975". A.J. Kreuger and R.A. Minzner, NASA Document x-912-74 (1974).
- (f) Reference (c), above. Recently, Cox^(g) has investigated the absorption spectrum of HNO_2 and has estimated rate coefficients for the photolysis of HNO_2 from that data and solar photon fluxes at each altitude: at 20 km $k_8 \sim 1.2 \times 10^{-3} \text{ sec}^{-1}$; at 30 km $k_8 \sim 1.4 \times 10^{-3} \text{ sec}^{-1}$. Both values are 24 hour averages.
- (g) R.A. Cox and R.G. Derwent, Journal of Photochemistry 6, 23-34 (1976/77).

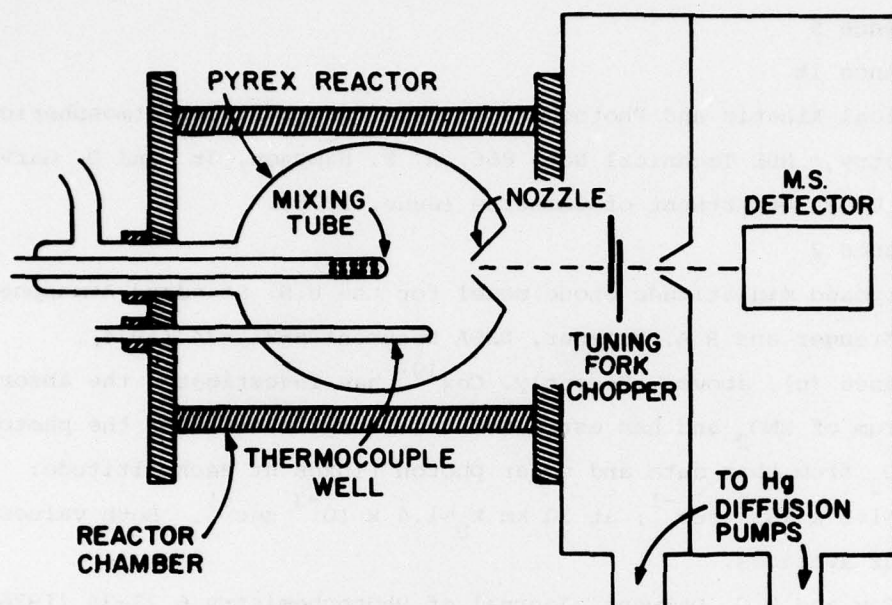
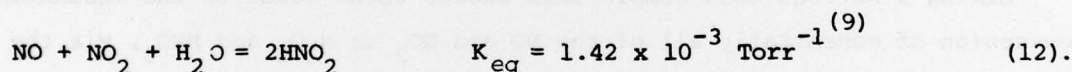


Figure 1. Schematic representation of the experimental apparatus.

The modulated ion signal was detected by a lock-in amplifier.

With the exception of N_2O_5 , the parent mass peaks of all reactants and products could be observed with the mass spectrometer. The observed relative ion intensities in the fragmentation patterns of pure nitrous and nitric acids are: $I(47 \text{ amu}) = 1.0$, $I(46 \text{ amu}) \leq 0.23$, $I(30 \text{ amu}) \leq 4.0$; and $I(63 \text{ amu}) = 1.0$, $I(46 \text{ amu}) = 46.3$, $I(30 \text{ amu}) = 11.6$, respectively. The fragmentation pattern for nitrous acid could not be determined in the static system employed in this work because it existed only in the presence of large excesses of NO and NO_2 , which have prominent mass peaks at 30 amu and 46 amu, respectively. The numbers presented above were obtained from flow measurements.^(8b) The observed relative ion intensities in the fragmentation pattern of ozone are $I(48 \text{ amu}) = 1.0$, $I(32 \text{ amu}) = 0.46$, and $I(16 \text{ amu}) = 0.072$. The detector as described yielded a signal-to-noise ratio of 1.0 with a 1 second time constant at reactor concentrations of $\sim 3 \times 10^{-4}$ Torr for nitrous acid and ozone, and $\sim 3 \times 10^{-3}$ Torr for nitric acid.

Ozone was prepared by electric discharge of oxygen and was stored on silica gel at -78°C after the excess oxygen was pumped off. Nitrous acid was prepared in equilibrium with NO, NO_2 and water in a 2-liter bulb. The HNO_2 concentration in the bulb was calculated from the equilibrium constant for reaction (12):



Typical concentrations at equilibrium in the storage bulb were $[NO] = [NO_2] = 2\text{-}6$ Torr; $[H_2O] = 3\text{-}8$ Torr; $[HNO_2] = 0.2\text{-}0.5$ Torr. The equilibria involving N_2O_4 and N_2O_3 were not included in the calculations as they are not significant at these concentrations. Nitric acid for use in the determination of its fragmentation pattern was prepared as a high purity (>90%) gas by reacting potassium nitrate with outgassed concentrated sulfuric acid under vacuum.

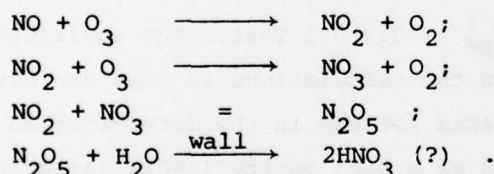
Experiments were performed at two reactor temperatures, 226° and 300°K . The room temperature experiments were carried out as follows. High purity ozone (>90% as determined by the pressure increase accompanying electric discharge decomposition of a small portion of the sample) was introduced into the reactor from the silica gel trap at pressures up to ~ 12 Torr. The reactor was then pressurized with Ar (Matheson Ultra High Purity) to 16 Torr total pressure as measured by a calibrated pressure transducer. An aliquot of the equilibrium

HNO_2 mixture was introduced into a calibrated 12 cm^3 volume which was then pressurized to one atmosphere with Ar. The resulting sample was injected into the reactor, and the HNO_2 decay was monitored at 47 amu. The initial nitrous acid concentration in the reactor was 0.002-0.005 Torr. When the nitrous acid decay was complete, the concentrations of the remaining materials were determined from the intensities of the observed mass peaks.

For the experiments carried out at 226°K , the procedure was somewhat different. The reactor was first cooled below the experimental temperature by passing gaseous nitrogen, precooled to near 78°K , through the reactor. At temperatures as low as 200°K , the reactor warmed up at a rate of $2^\circ\text{minute}^{-1}$ after the nitrogen flow was stopped. While the reactor was warming up to 226°K , the nitrous acid mixture was introduced into it as outlined above. Ozone, at the desired concentration, was stored in a second bulb pressurized to 40 Torr with Ar. When the reactor temperature reached 226°K , the ozone in the storage bulb was injected into the reactor, with the time for complete injection of the ozone sample being less than 3 seconds. The data acquisition time was less than two minutes, during which time the temperature rise was never more than 5° .

III. Results and Discussion

Mixing a nitrous acid sample with excess ozone leads to the instantaneous conversion of essentially all of the NO and NO_2 to N_2O_5 and HNO_3 , via the following reactions:



Thus, the expected equilibrium HNO_2 concentration in the reactor in the presence of excess ozone is near zero, as determined by equilibrium (12). The HNO_2 concentration can decay to its near zero final value by two established reactions in addition to the possible reaction between HNO_2 and ozone. These reactions are: (a) HNO_2 self-decomposition via reaction (-12). This reaction has been found to be heterogeneous, ^(8a) with a rate of decomposition which is very sensitive to the condition of the reactor walls; (b) reaction of nitrous

acid with nitric acid via reaction (13).^(8b) This reaction may have both



heterogeneous and homogeneous components. The self-decay rate of HNO_2 can be decreased by more than a factor of 100 in the absence of O_3 by pretreating the reactor with ~ 5 Torr of H_2O , which is then pumped out prior to the experiment. Pretreatment with as little as 0.5 Torr of O_3 immediately reactivates the surface.

300°K Results. In order to evaluate the contributions to HNO_2 decay from all the possible reaction paths, a series of experiments was carried out with variations in ozone, and coincidentally, nitric acid concentrations. In addition, since water was always present during the experiments from the HNO_2 equilibrium mixture, a comprehensive study of its effect on the HNO_2 decay rate over a wide range of water concentrations was conducted.

The decay of HNO_2 in the presence of excess ozone is shown in Fig. 2 for a typical run. There was a rapid (~ 1 second) buildup of HNO_2 resulting from its introduction into the reactor, a 2-4 second period during which the HNO_2 concentration remained stable, and then a continuous decay with a half-life of 15-25 seconds. The magnitude of the decay in the 47 amu mass peak after ozone injection was equal, within experimental error, to the observed magnitude of the initial nitrous acid signal when the equilibrium aliquot was injected in the absence of ozone. This indicates that the observed decay in the 47 amu peak after mixing with ozone is a result of the disappearance of HNO_2 . The HNO_2 injection was accompanied by an immediate (<1 second) drop in the ozone concentration resulting from the reactions which form N_2O_5 , and the mass peaks at 46 amu and 30 amu were simultaneously converted into a ratio characteristic of N_2O_5 . The nitric acid concentration slowly increased due to the $\text{N}_2\text{O}_5 - \text{H}_2\text{O}$ reaction, with the rate being dependent on experimental conditions.

The HNO_2 decays were always pseudo-first order in HNO_2 concentration for at least the first 75% of the decay. Representative exponential decays are shown in Fig. 3. The pseudo-first order rate constants, k' , derived from the exponential decay portion of each of the experiments, are presented in Table 2. Also shown are the ozone, water and nitric acid concentrations determined after the HNO_2 decay was complete. In the Table, the individual groups of

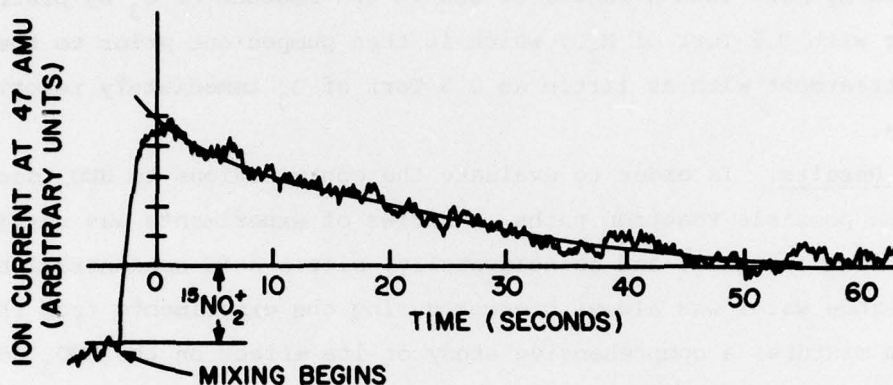


Figure 2. The decay of HNO_2 monitored at its parent mass peak (47 amu), in the presence of excess ozone at 300°K. The initial reactor concentrations were: $[\text{O}_3] = 10.4$ Torr; $[\text{HNO}_2] \sim 0.003$ Torr; $[\text{H}_2\text{O}] \leq 0.2$ Torr; $[\text{Ar}] = 14.5$ Torr. The increase in the baseline after the addition of the nitrous acid mixture arose from an increase in N_2O_5 and/or HNO_3 , both of which have a fragment peak at 47 amu due to $^{15}\text{NO}_2^+$.

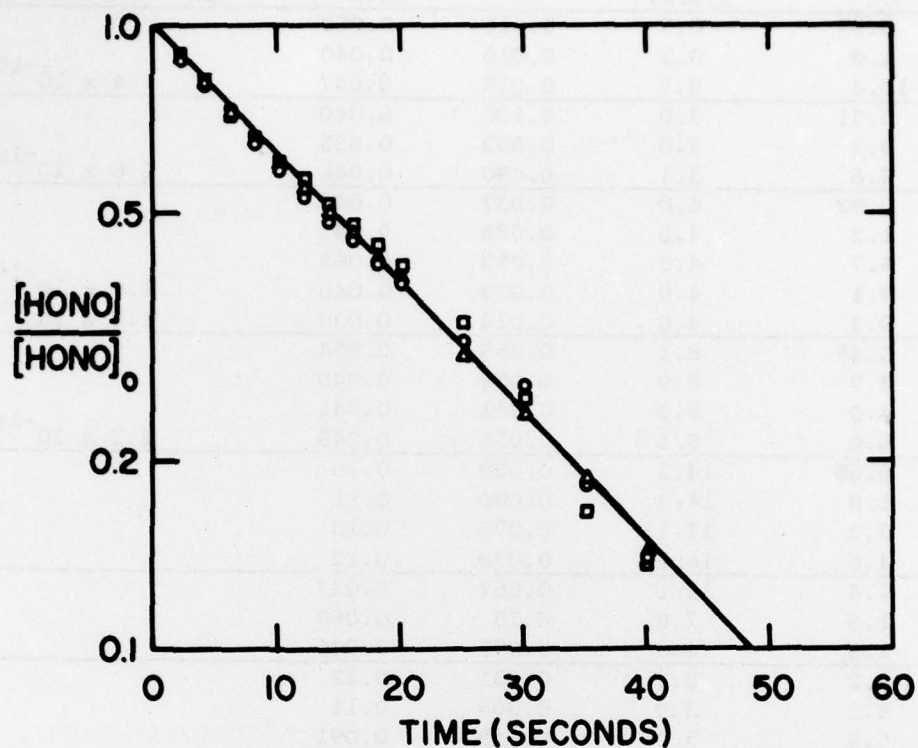


Figure 3. The exponential decay of HNO_2 in the presence of excess O_3 at 300°K (Series A in Table 2). $[\text{O}_3] = 10.4 \text{ Torr}$ (\square); $[\text{O}_3] = 6.0 \text{ Torr}$ (\circ); $[\text{O}_3] = 0.97 \text{ Torr}$ (Δ). In each case, $[\text{HNO}_2]_0 = 0.003 \text{ Torr}$ and $[\text{H}_2\text{O}] = 0.2 \text{ Torr}$. The total pressure for each run was increased to 25 Torr with Ar. The solid line represents the best fit to all three sets of data with a pseudo-first order rate constant $k = 0.047 \text{ sec}^{-1}$.

Table 2 - Decay of HNO_2 in the Presence of O_3 *

T (°K)	$[\text{O}_3]$ (Torr)	$[\text{H}_2\text{O}]$ (Torr)	$[\text{HNO}_2]$ (Torr)	k' (sec^{-1})	k_1^{**} ($\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$)
300	0.97	0.5	0.016	0.050	
(A)	6.0	0.2	0.016	0.040	
	10.4	0.2	0.015	0.047	1.4×10^{-19}
300	0.51	3.0	0.100	0.040	
(B)	3.2	3.0	0.093	0.035	
	8.6	3.1	0.090	0.046	1.6×10^{-19}
300	0.82	4.0	0.037	0.040	
	1.2	4.2	0.028	0.043	
(C)	6.7	4.0	0.055	0.063	1.6×10^{-19}
	9.1	4.0	0.039	0.048	1.0×10^{-19}
	9.2	4.0	0.014	0.030	
300	0.45	8.1	0.055	0.054	
(D)	3.2	8.0	0.053	0.040	
	4.0	8.3	0.061	0.041	
	6.0	8.1	0.056	0.045	2.3×10^{-19}
300	0.66	14.2	0.088	0.10	
	1.0	14.3	0.080	0.11	
(E)	2.2	14.1	0.078	0.10	
	4.5	14.7	0.070	0.12	
300	1.4	14.1	0.067	0.037	
(F)	1.5	7.8	0.10	0.060	
	1.5	4.0	0.097	0.046	
300	6.2	0.2	0.031	0.12	
	6.2	3.0	0.065	0.11	
(G)	5.8	5.0	0.049	0.091	
	5.3	6.3	0.053	0.078	
	5.6	6.8	0.079	0.10	
	5.5	13.5	0.050	0.060	
226	1.5	0.2	0.1	0.31	
(H)	1.5	0.2	0.1	0.15	
	9.8	0.2	0.1	0.22	5.1×10^{-19}
	14.0	0.2	0.1	0.37	6.2×10^{-19}
226	0.4	0.2	0.1	0.11	
(I)	1.2	0.2	0.1	0.21	
	4.2	0.2	0.1	0.21	
226	0.3	0.2	0.1	0.34	
(J)	6.3	0.2	0.1	0.30	

* The total pressure was 25.0 Torr at 300°K and 22.0 Torr at 226°K.

Typical initial reactor concentrations were: $[\text{HNO}_2] = 0.003\text{--}0.005$ Torr
 $[\text{NO}] = 0.03\text{--}0.06$ Torr; $[\text{NO}_2] = 0.02\text{--}0.04$ Torr. Each group of data was obtained during one day.

** These rate constants were derived by assuming that k' arises totally from reaction (1).

data were taken during one day in order to minimize the effects of changes in the reactor surface condition.

The effect of water is best illustrated by data series G in Table 2, in which the water content was varied by a factor of 75 while ozone and HNO_3 were maintained essentially constant. From the values of k' in this series of data, it can be seen that water does not systematically affect the HNO_2 decay rate in the presence of O_3 .

The effect of ozone concentration on the HNO_2 decay is also presented in Table 2 at several initial reactant concentrations and is shown graphically in Fig. 3 for the runs with the lowest water concentration (series A, Table 2). The data in Fig. 3, obtained for ozone concentrations between 0.97 and 10.4 Torr, can be fitted by the same exponential decay curve, within a 10-15% scatter. As presented in Table 2, the same result was obtained for HNO_2 decay measured with a 17-fold variation in ozone concentration in the presence of 3 Torr of water (series B), with a 13-fold ozone concentration variation in the presence of 8 Torr of water (series D), and with a 7-fold ozone concentration variation in the presence of 14 Torr of water (series E). This is strong evidence that any reaction between ozone and nitrous acid is not homogeneous and bimolecular under our experimental conditions.

The data presented above cannot be used to rule out the possibility that the reaction is zero order in ozone concentration. This would probably occur only if the reaction were heterogeneous and if the ozone concentration were sufficiently high to saturate the active surface sites. At the ozone pressures employed, 0.9-10 Torr, this seems unlikely. In addition, the nitrous acid decay rates observed in these experiments were of the same order of magnitude as those observed for the heterogeneous self-decay of HNO_2 in the absence of ozone and for the decay of HNO_2 in the presence of the HNO_3 concentrations reported in Table 2. Therefore, it is also unlikely that the decay of HNO_2 in the presence of ozone is a result of a heterogeneous reaction between HNO_2 and ozone. Thus, the experiments show no definitive evidence for a reaction between ozone and nitrous acid at room temperature.

226°K Results. A number of experiments were also performed at 226°K (series H, I, and J in Table 2). In these experiments the water present (≤ 0.2 Torr) came only from the equilibrium HNO_2 mixture. The HNO_2 decays were exponential over the first 80% of the decay, and they were independent ($\sigma \approx 50\%$) of the ozone concentration from 0.4 to 19 Torr. However, the pseudo-first order

decays were an average of a factor of 4 faster than those recorded at room temperature. The reason for the increase in the HNO_2 decay is not understood, although it is presumed to arise from changes in the effect of surface activity on reactions (12) and (13). In any event, the invariance of the decay rate over a factor of 50 variation in ozone concentration demonstrates that any reaction between ozone and nitrous acid cannot be homogeneous and bimolecular at 226°K, in agreement with the room temperature data.

IV. Upper Limit to the Bimolecular Rate Constant for the $\text{HNO}_2\text{-O}_3$ Reaction

As has been described above, the HNO_2 decay rate is independent of the ozone concentration at 226° and 300°K. Therefore, the data in Table 2 can only be used to determine an upper limit to the homogeneous, bimolecular rate constant for reaction (1). Assuming that all of the HNO_2 decay arises from reaction (1), the rate constant for the assumed bimolecular reaction can be obtained from the measured pseudo-first order rate constant and the known ozone concentration, $k_1 = k'/[\text{O}_3]$. Table 2 includes the upper limit values to k_1 calculated from experiments at the highest ozone concentrations. The values so derived are reasonably reproducible and the smallest values at 300° and 226°K are $1 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ and $5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively. Since, at both temperatures, a 10-50 fold variation in ozone concentration brings about a maximum 25-50% variation in the observed decay rate of HNO_2 , these upper limits are conservative.

V. Implications for Stratospheric Chemistry

The chemistry of NO_x compounds in the stratosphere is summarized in Table 1.^(1-3,5) The reactions of NO_3 and N_2O_5 have not been included in the calculations because they are not well understood.^(2,5) If reactions (1) and (2) are not included, the mechanism outlined in Table 1 predicts⁽⁵⁾ an NO density profile which is essentially constant for the 16 to 40 km region of the stratosphere. However, Schiff⁽⁵⁾ has recently demonstrated that the inclusion of reactions (1) and (2), with sufficiently large rate constants, would convert much of the NO and NO_2 into nitric acid, resulting in up to a 10-fold decrease in NO and NO_2 in the 20 km region. This would result in a drop in the ozone destruction rate by NO_x compounds by about a factor of 2 in that region.⁽¹⁰⁾

Using steady state assumptions for NO, NO₂, HNO₂, and HNO₃, the following relationships between the various NO_x compounds can be derived from the mechanism presented in Table 1 (see Schiff⁽⁵⁾).

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_3 [\text{O}_3] + J_9 [\text{HNO}_3] / [\text{NO}] + k_{11} [\text{HO}_2]}{k_4 [\text{O}] + J_5 + k_2 [\text{HO}_2] + k_7 [\text{OH}]} \quad (\text{I}')$$

Due to the small effect of many of the terms, (I') reduces to

$$\frac{[\text{NO}_2]}{[\text{NO}]} = \frac{k_3 [\text{O}_3]}{k_4 [\text{O}] + J_5} = a \quad (\text{I})$$

$$\frac{[\text{HNO}_2]}{[\text{NO}]} = \frac{ak_2 [\text{HO}_2] + k_6 [\text{OH}]}{J_8 + k_1 [\text{O}_3]} = b \quad (\text{II})$$

$$\frac{[\text{HNO}_3]}{[\text{NO}_2]} = \frac{k_7 [\text{OH}] + R(k_2 [\text{HO}_2] + k_6 [\text{OH}]/a)}{J_9 + k_{10} [\text{OH}]} = c \quad (\text{III})$$

Where

$$R = \frac{k_1 [\text{O}_3]}{k_1 [\text{O}_3] + J_8} \quad (\text{IV})$$

Equations (I)-(IV) can be evaluated if all the rate constants and reactant concentrations are known. The best estimates for these values are presented in Table 1 for altitudes of 22 km and 30 km. The values of equations (I) - (IV) are given in Table 3 as a function of the rate constant for reaction (1). In these calculations, we have used the value of k_2 ($2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$) chosen by Schiff.⁵

The fractional distribution of the four NO_x species under discussion can be obtained from the data in Table 3 by solving the set of simultaneous equations, (I) - (III), and setting the total NO_x equal to 1.0. The calculated

Table 3 - Evaluation of Equations (I) - (III) as a Function of the Value of k_1

	$k_1^* = 10^{-19}$	10^{-18}	10^{-16}	10^{-14}
Altitude = 22 km				
$\frac{[\text{NO}_2]}{[\text{NO}]}$	4.2	4.2	4.2	4.2
$\frac{[\text{HNO}_2]}{[\text{NO}]}$	0.131	0.129	0.0586	0.00105
$\frac{[\text{HNO}_3]}{[\text{NO}_2]}$	2.38	2.81	24.0	41.3
R	0.0012	0.012	0.55	0.99
Altitude = 30 km				
$\frac{[\text{NO}_2]}{[\text{NO}]}$	1.7	1.7	1.7	1.7
$\frac{[\text{HNO}_2]}{[\text{NO}]}$	0.0538	0.0535	0.0368	0.00114
$\frac{[\text{HNO}_3]}{[\text{NO}_2]}$	0.417	0.440	2.16	5.83
R	0.00046	0.0046	0.32	0.99

* k_1 has the units of $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

results are presented in Table 4 at altitudes of 22 km and 30 km as a function of the value of k_1 . There is no effect on the relative NO_x concentrations when k_1 values below 1×10^{-19} are employed, and the calculations indicate that the maximum perturbation on the NO_x concentrations, which occurs at 22 km, would be less than 5% using the measured upper limit to k_1 , $5 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This is a very small perturbation and indicates that the effect of reactions (1) and (2) will not be large unless k_2 is much larger than $2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. The value of k_2 has not yet been directly determined, and, in fact, there is evidence that pernitric acid, not nitrous acid, is the primary reaction product.⁽¹¹⁾ This fact, coupled with a recent indirect determination⁶ of k_2 , points to a formation rate for nitrous acid via reaction (2) which is slower than that used in the present calculations. If this is correct, the effect of reactions (1) and (2) in the stratosphere would further decrease in importance. Thus, current evidence strongly suggests that the homogeneous, bimolecular reactions (1) and (2) have a negligible effect on the chemistry of the stratosphere.

Table 4 - Fractional Distribution of NO_x Among Its Major Components as a Function of the Value of k_1

	$k_1^* = 10^{-19}$	10^{-18}	10^{-16}	10^{-14}
Altitude = 22 km				
NO	6.5(-2) **	5.8(-2)	9.4(-3)	5.6(-3)
NO_2	2.7(-1)	2.5(-1)	4.0(-2)	2.4(-2)
HNO_2	8.5(-3)	7.5(-3)	5.5(-4)	5.9(-6)
HNO_3	6.5(-1)	6.9(-1)	9.5(-1)	9.7(-1)
Altitude = 30 km				
NO	2.9(-1)	2.9(-1)	1.6(-1)	7.9(-2)
NO_2	4.9(-1)	4.9(-1)	2.7(-1)	1.3(-1)
HNO_2	1.6(-2)	1.5(-2)	5.7(-3)	9.0(-5)
HNO_3	2.0(-1)	2.1(-1)	5.7(-1)	7.9(-1)

* k_1 has the units of $\text{cm}^3 \text{molecule}^{-1} \text{sec}^{-1}$

**6.5(-2) = 6.5×10^{-2}

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